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Outline of Proposed Methodology Kroll Process Waste Evaluation

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Background

At the request of U.S. Environmental Protection Agency (EPA) Region 8, the National Enforcement Investigations Center (NEIC) has been asked to sample and evaluate magnesium chloride reaction products from the Kroll process used by Western Zirconium at their Ogden, Utah facility in the production of hafnium and zirconium metals. The evaluation would be to determine if any of these materials has any of the reactivity properties given in 40 Code of Federal Regulations (CFR) Section 261.23. Those relevant properties in order of appearance in that regulation are as follows: reacts violently with water; (2) forms potentially explosive mixtures with water; (3) when mixed with water, generates toxic gases, vapors or fumes in quantity sufficient to present a danger to human health and the environment; and (4) and is sulfide bearing and, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment.

Approach

The regulations do not specify analytical processes to examine the properties in question. The background document¹ (p. 23) provides that, “The generator is free to conduct any tests which aid him in assessing whether his waste fits within the prose definition of reactivity. The Agency is not bound in any way by these tests and will make its assessment of whether a waste is reactive by reference to the prose definition.” As a means to demonstrate the properties, the NEIC plans to conduct the following testing:

For property (2), reacts violently with water, samples of the waste will be mixed with water in an open 100 mL test tube. The temperature of the mixture will be monitored and the headspace above the mixture analyzed for hydrogen and hydrogen sulfide. The method for assessing water reactivity according to Mason and Cooper² will be used. For the 10 gram sample and the 10 gram water test, water vaporization will be determined gravimetrically and thermochemical computations will be conducted to derive the heat of mixing for comparison to the NFPA 704 guidance.

¹ Background Document – Resource Conservation and Recovery Act Subtitle C – Identification and Listing of Hazardous Waste - § 261.23 – Characteristic of Reactivity, EPA, May 2, 1980.

² Mason, C.M; Cooper, J.C. Classification of Hazards of Materials – Water Reactive Materials and Organic Peroxides, Report No. TSA-20-72-2, Department of Transportation, Office of Hazardous Materials, Washington, D.C. NTIS Number PB-209 422, March 1972.

For property (3), forms potentially explosive mixtures with water, three scenarios are contemplated and three approaches are outlined for use:

- A sample of the waste will be mixed with water in an apparatus that captures the gas evolved and the total gas production will be measured volumetrically. The procedures outlined by the United Nations³ N.5, “Test method for substances which in contact with water emit flammable gases” will be used as guidance, however, the one liter per kilogram per hour threshold is inappropriate. Hydrogen concentrations will be measured using gas chromatography with thermal conductivity detection. The hydrogen concentration will be used to estimate an elemental magnesium concentration.
- A sample of the waste will be mixed with water (200 gram waste and 200 gram water) in an epoxy lined one gallon paint can with a loosely fit lid and the static or semistatic headspace will be monitored for hydrogen and hydrogen sulfide for 30 minutes. The lid is equipped with 2 septum ports constructed of ¼ stainless bulkhead fittings to facilitate simultaneous sampling for hydrogen and hydrogen sulfide. The headspace concentrations will be compared to NIOSH, OSHA and EPA health based standards.

The explosivity of the gases produced will be examined using a high potential electric igniter as means of initiation.

- The headspace for the Mason and Cooper testing for the 10 gram sample and 10 gram water test will be analyzed for hydrogen and hydrogen sulfide.

For property (4), is sulfide bearing, the approach will be to add water or acidify the sample, collect a portion of the hydrogen sulfide formed, react with a basic media and then measure the sulfide product titrimetrically or using FIA/membrane gas diffusion/pulsed amperometry.⁴ Conway diffusion cells containing 0.1 normal (N) sodium-hydroxide-trapping solution may be used in this process. Lead acetate paper may be used to preliminarily identify the presence of sulfide above or in aqueous or acid mixtures with the sampled materials.

For property (5), acid-releasable sulfide can be measured by adding water or acidifying measured quantities of solid samples placed in Conway diffusion cells also containing 0.1 normal (N) sodium-hydroxide-trapping solution. pH conditions are controlled to just above 2 in this process by predetermining the amount and concentration of hydrochloric acid to be added to the sample aliquot utilized. Hydrogen sulfide concentrations produced during the container test as above may be used in assessing produced concentrations over time. This will be accomplished by pulling a measured quantity of the gas from the

3 United Nations Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria (4th ed.), New York and Geneva, 2002, ST/SG/AC, 10/11/Rev4, ISBN 92-1-139087-7.

⁴ Milosavijevic, E.B.; Solujic, L., Hendrix, J.L., Nelson, J.H. Flow Injection Gas Diffusion Method for Preconcentration and Determination of Trace Sulfide, *Anal. Chem.* 1988, 60: 2791-2796.

headspace of the container into a syringe containing sodium hydroxide absorbing solution and again measuring the sulfide product by similar methods.

X-ray diffraction may be used to identify crystalline phases in the materials. X-ray fluorescence spectrometry may be used to determine magnesium and chloride and other elements present.